

Seasonal Rainfall Effects on Pesticide Leaching in Riverside, California

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

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1220 N Street, Sacramento, California 95814

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BY

Rosemary H. Neal, Roberto R. Teso, Theodore **Younglove¹**, and David L. Sheeks, III. California Department of Pesticide Regulation, Trailer 14, University of California, Riverside, CA 92521, and ¹Statewide Air Pollution Research Center, University of California, Riverside, CA 9252 1.

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ENVI RONMENTAL HAZARDS ASSESSMENT PROGRAM

Abstract

The objective of this study was to investigate the extent to which precipitation affects the mobility of pesticides in a sandy loam soil which received no additional irrigation. During a four month period, 172 mm of rain fell on the experimental plots to which **ordram**, simazine and carbofuran had been applied at a rate of **0.001kg** active ingredient **m**-2. A qualitative evaluation of soil cores taken upon conclusion of the study indicated that the bulk of the pesticide applied was not detectable below a depth of 0.76 m. The use of two sampling techniques, split barrel mobile drill auger vs bucket-auger, to collect the samples, enabled a comparison which indicated that the use **oi** a bucket-auger to collect contaminated samples in dry sandy soils, may not be the most appropriate method.

Acknowledgments

The authors wish to thank Cindy Garretson for performing organic carbon analyses on the samples generated from this study, and seasonal personnel, including Holly Haggerty and Allen Lee, for their contribution to particle size analysis and field work, respectively. Thanks are also extended to Dr. Patrick McCool and his staff for services rendered under CDFA Contract #90-0276 at the Statewide Air Pollution Research Center at UC Riverside.

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Introduction

The efficacy of pesticides in agricultural systems is impacted by a number of factors, some of which may be controlled by the intervention of management practices. In general, a chemical's ability to leach, and its potential for groundwater contamination, will be affected by formulation (eg., Fur-midge, 1984) and mode of pesticide application, interaction of the chemical with soil components (eg. Weed and Weber, 1974; Calvert, 1980), and the volume of water applied to the land surface (eg. Jury, 1986). Rainfall, as a component of irrigation management used in California, will interact with each of these factors, and will result in a wide variation of chemical distribution within the soil profile (eg. Himel et al. 1990; Leonard, 1990). The mechanisms involved in the interactions between water and a specific pesticide will be very similar regardless of the source of the water, however, the timing, intensity, and the amount of precipitation will play a significant role in the eventual behavior of the chemical in the soil environment, For example, the duration between the application of a pesticide and a rainfall event will affect such factors as the rate of pesticide decomposition, photo-degradation, and volatilization, and the extent to which the remaining pesticide will be incorporated in the soil. Once rain has fallen, the quantity of precipitation will influence tke depth to which a chemical may be carried, the partition of the chemical between soluble and sorbed phases, and hence its availability to the biological target,

In most instances in California, precipitation constitutes only a small fraction of the total amount of water applied to agricultural crops and, therefore, timing rather than volume is a more viable concern. Studies reported in the literature on the effects of rainfall on resocide movement in soils are scarce, particularly in reference to California, and this may be attributed to the comparatively small of rainfall compared to the amount applied through irrigation, the latter having been investigated extensively over the last 15 years, Milburn et al.(1990) examined the effects of rainfall on the movement of nitrates in systematically

tilled potato fields in New Brunswick, Canada. These authors observed nitrate leaching in Typic Cryorthod soils (compact basal till) of the region to be highly dependent on the timing of the rainfall event with respect to fertilizer application, and the importance of preferential flow through macropore systems as a means of rapidly moving nitrate through the soil profile. Similar results were reported by Isensee et al. (1990) who investigated pesticide leaching to shallow ground water at a site in Maryland. Atrazine, alachlor, cyanazine, and carbofuran were applied to a Typic Fluvaquent and an Aquic Udifluvent soil, both silt loams, and the ground water monitored for residues and metabolites. Atrazine, and its metabolite diethylatrazine, were far more commonly detected in the ground water than the other three pesticides, with higher concentrations of all chemicals found in a shallower perched aguifer (<1.5m) compared to the deeper confined groundwater (<3m). Rainfall timing relative to pesticide application was critical to determining whether major leaching of pesticides occurred, with greater leaching occurring when rainfall quickly followed application. Unusually rapid pesticide leaching to depths beyond those predicted by classical transport theory was also observed, and presumed to be the result of macropore flow mechanisms (Isensee et al., 1990).

Shipitalo et al. (1990) examined the impact of initial storm effects on chemical transport in no-till soil, where extensive macropore systems had developed. Strontium bromide hexahydrate (SrBr₂.6H₂O) and atrazine were surface applied to undisturbed blocks of a Typic Hapludult soil, a silt loam, under laboratory conditions, and irrigated with simulated rain. The simulated rain followed two patterns. One set of samples was irrigated with an initial 5-mm application of rain immediately after pesticide application, and this was then followed two days later by 0.5h 30-mm simulated rain. The alternate set of samples did not receive the initial 5-mm application. The authors reported that the initial 5-mm rain event substantially reduced the amount of freshly applied SrBr₂ and atrazine which was subsequently leached through the macropore system, and they attributed this to a

mechanism in which the solutes were moved into the soil matrix and adsorbed, thereby reducing the potential for transport in macropores during subsequent rainfall events. The soils which did not receive the first 5-mm event, were more readily leached through the system of macropores. An earlier study, White et al. (1986) investigated, the leaching of bromacil and napropamide through large undisturbed cores of an Aquic Eutrochrept clay 'soil. Data indicated, that continuous leaching resulted in greater herbicide breakthrough than did a discontinuous regime, and this phenomenon was attributed to the diffusion of the herbicides into soil aggregates during the quiescent period of the latter regime. In addition, White et al. (1986) reported the effect of prewetting the soil was to reduce the amount of pesticide leached from the soil columns, in agreement with the later findings of Shipitalo et al. (1990).

Although there is little information in the current literature directly concerned with the effect of rainfall on chemical mobility in soils typically found under agricultural conditions in California, results reported in the studies cited above may be used to further the understanding of pesticide mobility. However, those studies which are published in the literature indicate that the rainfall component may affect the behavior of pesticides in soils, particularly in determining the amount of a chemical that may be leached into the soil profile. This study was designed to observe and characterize the effects of seasonal rainfall in Riverside Ca. on the distribution of three surface applied pesticides, carbofuran, ordram, and simazine, in replicated 3 m square soil plots. Three chemicals, ordram, carbofuran, and simazine, were chosen for this study, and were selected for the following reasons. Ordram was chosen because, at the time of the study, no residues of this chemical bave been detected in California ground waters, despite its considerable usage as a rice herbicide, and high solubility in water (880mg I-1. Farm Chemical Handbook, 1991). Rice fields are generally located on heavy clay soils, such as the Willows series (fine montmorillonitic, thermic, Typic Pelloxererts) found in the Sacramento Valley, and pesticide mobility in these

types of soils is limited owing to their relatively low porosity (Jury, 1986). Carbofuran, also used as a rice herbicide, was chosen because despite its relative insolubility (Farm Chemical Handbook, 1991) it has been detected in groundwater in the states of Maryland, New York, and Wisconsin (Cohen et al., 1986). A secondary objective of this study was, therefore, to investigate the behavior of both carbofuran and **ordram** in the more porous Hanford coarse sandy loam found at the University of California field station in Riverside. Finally, the inclusion of simazine in this study resulted from observations by Weaver et al. (1983) of residues of this chemical in ground water in the Fresno area, where it is used on crops grown on the Hanford series soils of the region.

Materials and Methods

Experimental Field Site

The experimental plots were set up at the field station of the University of California, Riverside. Three blocks were oriented lengthwise along a 37 m transect (Fig.1). Each block was 11 m in length, and was separated from each neighboring block by a 2 m buffer. Each block consisted of three 3 m square plots, surrounded by a 1 m buffer. The plots were prepared using a rotary cultivator, in order to minimize runoff and ponding. In order to accommodate the effects of extreme rainfall events, the plots were designed to allow runoff to move away from the experimental transect, and furrows were raised at the head end and along the sides of the plots to exclude irrigation and rainfall runoff effects from the surrounding area. The plots were situated on a Hanford coarse sandy loam (coarse-loamy, mixed, nonacid, thermic typic Xerorthents).

Soil Sampling

Two undisturbed background soil cores to a depth of 3.05 m were taken from between the blocks using a 1982 Mobile Drill, Model B-53, mounted on a 1982 International Harvester S1800, 4x4 cab and chassis. Hollow stem augers (1.52 m long, 0.086 m i.d., 0.203 m o.d.) containing a split barrel sampler were used in the drilling operation (Segawa et al., 1986, p26-29). The split barrel sampler contained three stainless steel liners (0.152 m long, 0.064 m o.d., 0.060 m i.d.), plus an additional 0.051 m of cutter shor. The cores were divided into the three 0.152 m increments (Fig.2), and each increment placed in a glass jar with a foil-lined lid, packed on dry ice, and placed in a refrigerated chamber located adjacent to the field site. The core samples were split, and a sub sample shipped to the contract laboratory (Cal-Lab) for pesticide residue determination. The remainder of the

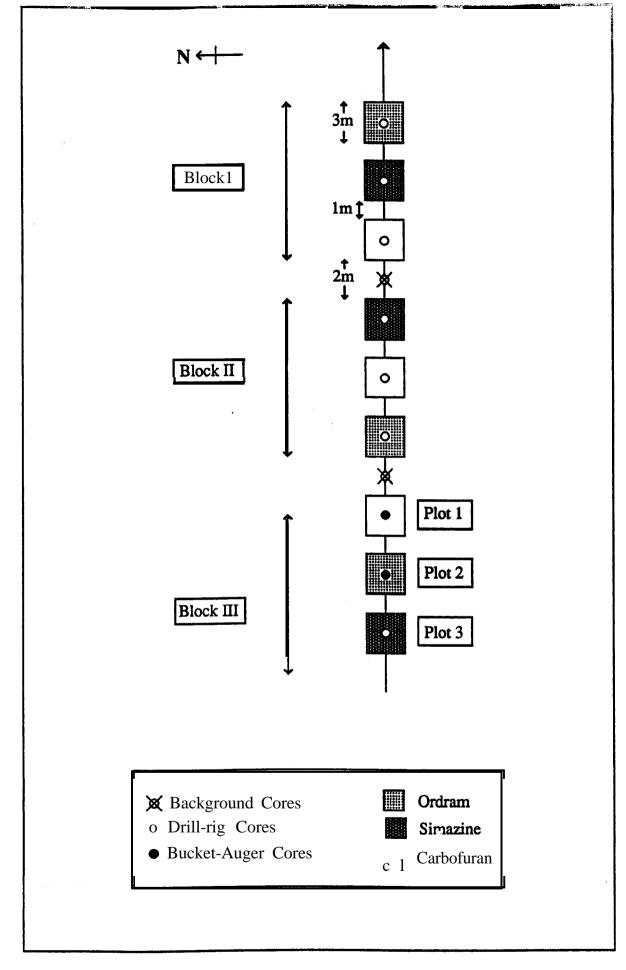
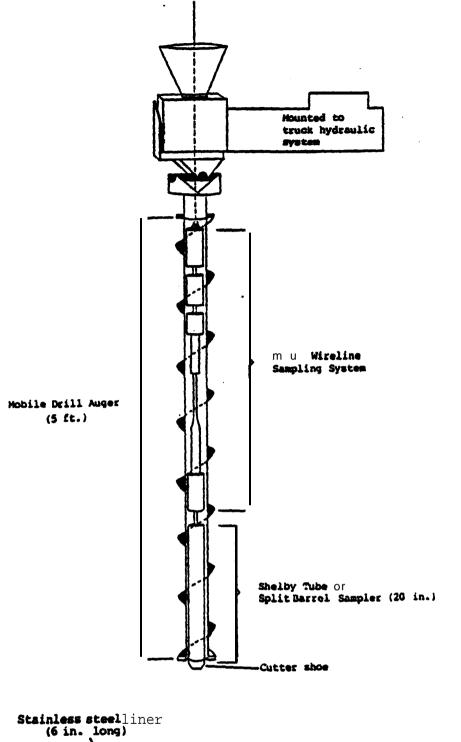


Figure 1. Experimental Plot Orientation at the Field Site



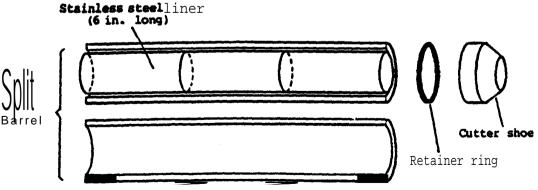


Figure 2. Mobile Drill Auger and Split Barrel Sampler (Segawa et al. 1986)

samples were examined for moisture content, particle size analysis (Bouyoucos, **1972)**, and organic carbon content (Walkley and Black, 1934).

One of three pesticides, carbofuran (emulsifiable concentrate), **ordram** (emulsifiable concentrate), or simazine (wettable powder), was applied to an individual randomly selected plot within each block (Fig.l). All pesticides were applied in liquid spray using a hand sprayer at a rate equivalent to 10 kg active ingredient (ai) hectare (ha) -1, and a water application rate of 187 liter (1) ha⁻¹. Precipitation was measured using an acrylic plastic All Weather Rain Gauge (Made to U.S. Weather Bureau specifications) located on-site adjacent to the experimental plots. Precipitation amounts were determined daily at 9.00 hrs PST and recorded in a log book. At the conclusion of the rainfall season (mid-April), the experiment was terminated. One 3.05 m soil core was removed from the center of each individual plot, as described above, and divided into 0.15 m increments (Fig.2), each of which were processed in the same manner as the background samples. Seven of the nine soil cores were sampled using the mobile drill auger, but the presence of overhead electrical wires prevented the safe use of the drilling rig in block III, plots 1 and 2 (Fig. 1), and these were sampled using a bucket auger (Acker Drill Co, Scranton, PA) method (Troiano, 1987).

Chemical Analyses

Soil samples were sent to the contract laboratory (ENSECO Cal-Lab) for processing and analysis. High-Performance Liquid Chromatography (HPLC) was used to determine concentrations of extractable simazine, carbofuran and **ordram** in the soil samples. HPLC has been used by Sparacino and Hines (1976) for the determination of carbofuran, and Byast (1977) for the determination of simazine in both soil and water samples. A method for determining **ordram** (thiobencarb) concentrations in soils was developed by CDFA and

Cal-lab in 1988 (Marade and Segawa). Detection limits of $5 - 20 \,\mu\text{g kg}^{-1}$ for ordram and simazine, and $5 - 10 \,\mu\text{g kg}^{-1}$ for carbofuran, were reported (Table 7).

The organic carbon content (Walkley and Black, 1934) of the soil samples, and their particle size analysis (Bouyoucos, 1972) were determined by Cindy Garretson at the CDFA Office in Fresno, CA, and Holly Haggerty at Trailer 14, SAPRC, UCR, respectively,

Results and Discussion

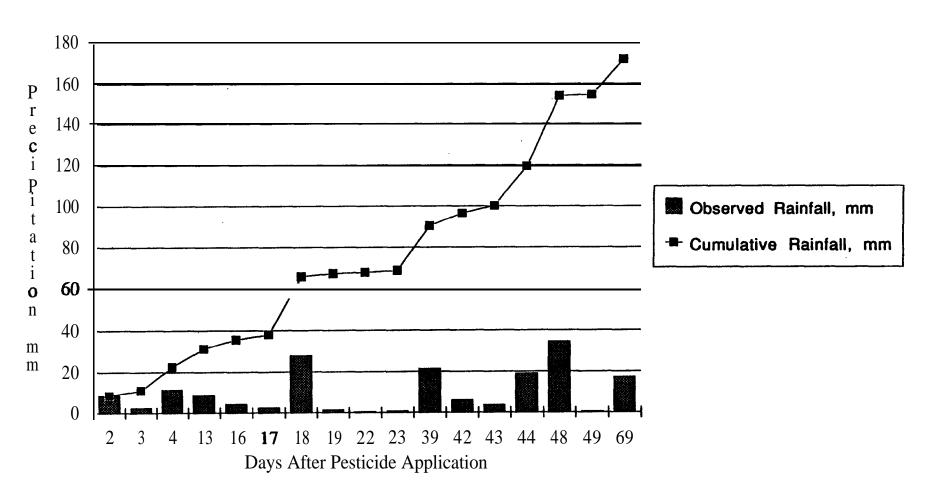
Rainfall Data

A total of 172 mm of rain fell on the experimental plots between the date of pesticide application (1/28/86) and the termination of the experiment (4/8/86). These data are shown in Figure 3 both as a function of the daily recordings, and as a cumulative total, and although the events were sporadic they can be divided into four discrete periods in which rain fell on the experimental plots. During the first four days after pesticide application a total of 23 mm of rain was observed, which was followed by a period of dry weather for 9 days. On the 13th day after pesticide application **9mm** of rain fell cumulating in 46 mm over an 1 **1-day** period. A third period of precipitation was recorded between the 39th and 49th days of the experiment, giving rise to a further 86 mm of precipitation. Finally, 17 mm was collected on the 69th day, and the experiment was concluded on day 70.

Organic Carbon Content and Particle Size Analysis

The percentage of organic carbon in the sampled soil profiles ranged between 1.6 and <0.1%, with the greatest amount and variation in the upper 6 inches of the soil (0.7 - 1.6%) (Table 1 and Fig.4). These values are within the range typical for Hanford series soils (SCS, 1973). Particle size analysis indicated the sand-sized fraction (0.053-2μm) is predominant in this soil with values ranging between 65 and 90%, increasing with depth (Tables 2, 3, & 4, and Fig.5). Clay- and silt-sized fractions decreased as a function of soil depth, with values dropping from 13.8±2.2% to 5.5±1.1% (clay), and 22.8±3.5% to 11.8±4.3% (silt). These values are also consistent with the ranges given by the Soil Conservation Service (1973) for this soil series.

Figure 3. Daily and Cumulative Precipitation Monitored Between 1/28/86 and 4/7/86.



<u>Table 1.</u> Percent Organic Carbon Found in Nine Soil Cores Sampled Upon Completion of the **Study†.**

Sampl	le		Block I			Block I			Block III	
#	Depth, m	Plot 1	Plot 2	Plot 3	Plot 1	Plot 2	Plot 3	Plot 1	Plot 2	Plot 3
										_
1	0.00 - 0.15	1.6	1.0	1.2	1.1	1.4	0.9	0.7	0.9	0.7
2	0.15 - 0.30	0.7	0.5	0.5	0.6	0.4	0.5	0.7	0.5	0.4
3	0.30 - 0.45	0.4		0.3		0.4	0.4	0.3	0.3	0.2
4	0.51 - 0.66	0.3	0.2	0.2	0.2	0.3	0.2	0.1	0.2	0.2
5	0.66 - 0.81	0.3	0.2	0.2	0.3	0.3	0.1	0.2	0.2	0.2
6	0.81 - 0.96	0.3	0.2	0.1	0.1	0.3	0.1	0.2	0.1	0.1
7	1.02 - 1.17	0.2	0.2	0.1		0.2	0.1	0.1	0.1	0.1
8	1.17 - 1.32	0.2	0.1	0.1	0.1	0.2	0.1	0.1	ND	0.1
9	1.32 - 1.47	0.2	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.1
10	1.47 - 1.68	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
11	1.52 - 1.83	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
12	1.83 - 1.98	0.1	0.1	0.1	0.1	0.1	ND	0.1	0.1	0.1
13	2.03 - 2.18	0.1	0.0	0.1	0.1	0.1	0.1	ND	0.1	ND
14	2.18 - 2.3 4	0.1	0.1	0.1		0.1	0.1	0.1	0.1	ND
15	2.34 - 2.49	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	ND
16	2.54 - 2.69	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	ND
17	2.69 - 2.84	0.1	ND	0.1		0.1	0.1	0.1	ND	ND
18	2.84 - 2.99	0.1		0.1	0.1	0.1	0.1	0.1	ND	ND

^{-- =} Missing Data ND = Not Detected † = For corresponding plot design refer to Fig. 1.

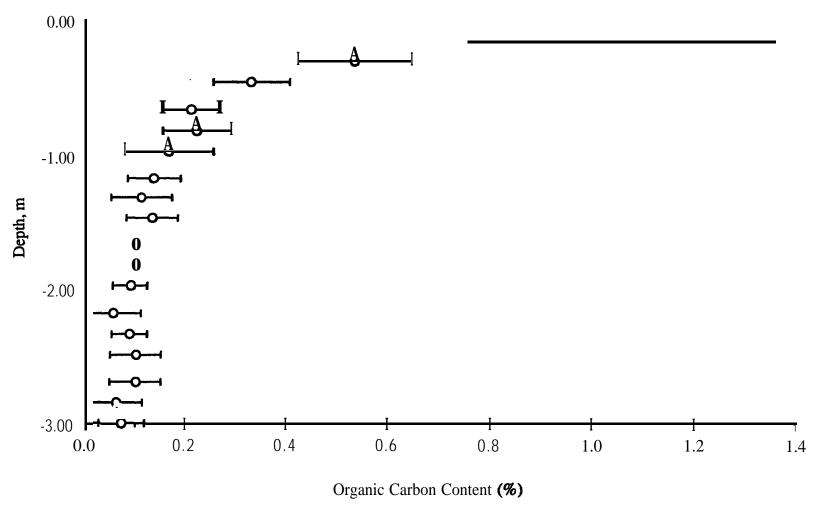


Figure 4. Distribution of Organic Carbon as a Function of Soil Depth. (Mean and S.D. of Nine Post-Study Soil Cores)

Pesticide Residue Analysis

A total of 198 soil samples were analyzed for pesticide residues. Thirty-six of the samples were derived from the background cores, and none had residue concentrations above the detection limits of the methods used (Table 5). Pesticide residues were detected in only 56 of the 162 soil core samples taken at the end of the experiment (34%) (Table 6). Because two of the nine plots (Block III, plots 1 & 2) were sampled using a different collection method (bucket auger vs. drill rig), these data may not be compared with the remaining seven. In the drill rig samples >95% of the pesticide residues for each core were detected in the upper 0.3 m of the soil profile, with the exception of Block I plot 1, where only 55% of the **ordram** residue was recovered above this depth because concentrations were several orders of magnitude lower than those found in Block II plot 3 (26 & 4800 µg **kg**⁻¹ respectively). Figure 6 represents the observed concentrations of pesticide residues reported for the nine soil cores sampled. The data have been expressed as a logarithmic function of chemical concentration in order to accommodate the wide spread of values. Simazine and carbofuran concentrations in the upper 12 inches of the soil core were reported as high as 21 000 µg kg⁻¹ and 13 000 µg kg⁻¹, respectively (Table 6). It should be noted, however, that during sampling a clearly identifiable smell of **ordram** residue was noted around a depth of 45 inches in the plots which had received ordram (Teso, pers.comm.).

Ten of the 198 soil samples analyzed were included in a Quality Assurance Program (Table 7.). Method spikes and method spike duplicates of the three pesticides, carbofuran, ox-dram and simazine, were added to the soil extracts at concentrations of 100 and 200 µg kg⁻¹. Recoveries ranged from 55 to 94% for ordram, 65 to 90% for simazine, and 70 to 105 % for carbofuran. In two of the samples tested, high sample analyte levels obscured

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<u>Table 2.</u> Particle Size Distributions of Three Soil Cores Sampled from Block I Upon Completion of the Study.

Samp	le	74	Plot 1-			Plot 2		*	Plot 3 -	
•		%Sand	%Silt	%Clay	%Sand	%Silt	%Clay	%Sand	%Silt	%Clay
#										
	Depth, m									
1	0.00 - 0.15	-	-	-	65.8	24	10.2	67.8	24	8.2
2	0.15 - 0.30	-	-	_	67.8	22	10.2	' 65.8	22	12.2
3	0.30 - 0.45	-	-	_	-		65.8	21.0	13	
4	0.51 - 0.66	-	-	-	65.8	22	12.2	55.8	28	16.2
5	0.66 - 0.81	-	-	-	51.8	26	16.2	55.8	28	16.2
6	0.81 - 0.96	-	-	-	62.8	25	12.2	62.8	25	12.2
7	1.02 - 1.17	-	-	-	71.8	20	8.2	69.8	22	8.2
8	1.17 - 1.32	-	-	-	69.8	22	8.2	74.8	17	8.2
9	1.32 - 1.47	-	-	-	77.8	14	8.2	81.8	12	6.2
10	1.47 - 1.68	-	-	•	71.8	21	7.2	80.8	13	6.2
11	1.52 - 1.83	-	-	-	67.8	26	6.2	79.8	14	6.2
12	1.83 - 1.98	-	-	-	71.8	18	4.2	81.8	9	3.2
13	2.03 - 2.18	-	-	-	83.8	12	4.2	75.8	14	10.2
14	2.18 - 2.34	-	-	•	87.8	10	2.2	69.8	20	10.2
15	2.34 - 2.49	-	-	-	-			75.8	14	10.2
16	2.54 - 2.69	-	-	~	75.8	18	6.2	71.8	22	6.2
17	2.69 - 2.84	-	-	~	85.8	7	7.2	67.8	24	8.2
18	2.84 - 2.99	-	-	•	•	-		85.8	10	4.2
1										

^{- =} Missing Data

16

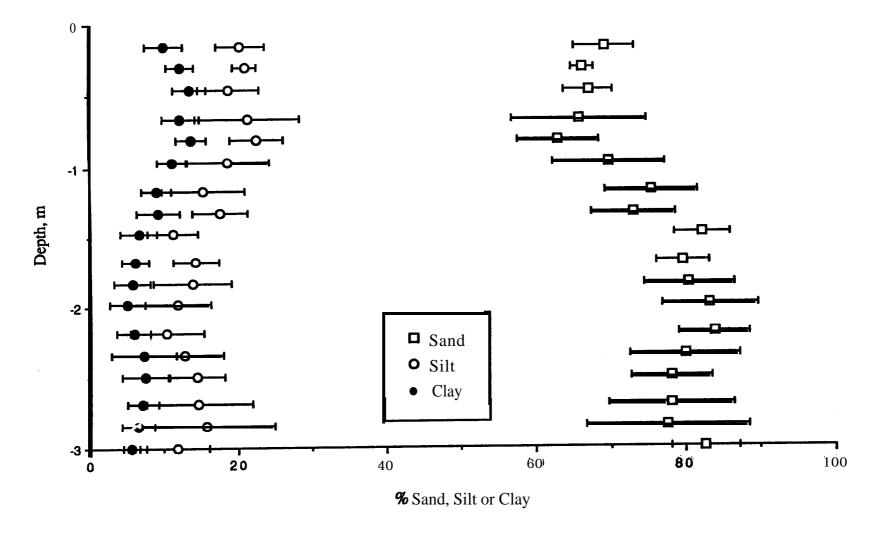
<u>Table 3.</u> Particle Size Distributions of Three Soil Cores Sampled from Block II Upon Completion of the Study.

Sampl	le		Plot 1-			Plot 2		*****	Plot 3 -	
_		%Sand		%Clay	%Sand	%Silt	%Clay	%Sand	%Silt	%Clay
#	Donth m									
	Depth, m									
1	0.00 - 0.15	69.8	16	14.2	78.6	16	5.4	67.8	22	10.2
2	0.15 - 0.30	64.8	23	12.2	68.6	22	9.4	61.8	18	14.2
3	0.30 - 0.45	-	23	12.2	66.6	22	11.4	68.8	19	12.2
4	0.51 - 0.66	63.8	24	12.2	70.6	20	9.4	51.8	28	14.2
5	0.66 - 0.81	63.8	$\frac{1}{2}$	14.2	66.6	20	13.4	69.8	20	10.2
6	0.81 - 0.96	62.8	23	14.2	82.6	10	7.4	15.8	$\overline{14}$	10.2
7	1.02 - 1.17	-			82.6	11	6.4	77.8	14	8.2
8	1.17 - 1.32	71.8	18	10.2	74.6	19	6.4	73.8	18	8.2
9	1.32 - 1.47	79.8	12	8.2	81.6	14	4.4	81.8	8	10.2
10	1.47 - 1.68	77.8	14	8.2	82.6	15	2.4	78.8	15	6.2
11	1.52 - 1.83	79.8	12	8.2	86.6	12	1.4	85.8	8	6.2
12	1.83 - 1.98	70.8	19	10.2	90.6	7	2.4	87.8	8	4.2
13	2.03 - 2.18	81.8	14	4.2	80.6	17	2.4	89.8	4	6.2
14	2.18 - 2.14				83.6	12	4.4	87.8	8	4.2
15	2.34 - 2.49	83.8	8	8.2	84.6	13	2.4	81.8	13	5.2
16	2.54 - 2.69	89.8	4	6.2	84.6	8	7.4	62.8	26	11.2
17	2.69 - 2.84		-		88.6	7	4.4	61.8	28	10.2
18	2.84 - 2.99	89.8	5	5.2	82.6	10	7.4	83.8	12	4.2

^{- =} Missing Data

<u>Table 4.</u> Particle Size Disributions of Three Soil Cores Sampled from Block III Upon Completion of the Study.

Samp	le		Plot 1-			Plot 2			Plot 3 -	
~ ·		%Sand	%Silt	%Clay	%Sand	%Silt		%Sand	%Silt	%Clay
#										
	Depth, m									
1	0.00 - 0.15	68.8	19	12.2	67.8	22	10.2	67.6	21	11.4
2	0.15 - 0.30	64.8	21	14.2	65.8	21	13.2	65.6	20	14.4
3	0.30 - 0.45	61.8	23	15.2	69.8	17	13.2	70.6	12	17.4
4	0.51 - 0.66	61.8	23	15.2	67.8	21	11.2	84.6	6	9.4
5	0.66 - 0.81	63.8	22	14.2	69.8	18	12.2	58.6	26	15.4
6	0.81 - 0.96	75.8	14	10.2	67.8	20	12.2	68.6	19	12.4
7	1.02 - 1.17	71.8	17	11.2	69.8	18	12.2	84.6	6	9.4
8	1.17 - 1.32	80.8	11	8.2	61.8	22	16.2	76.6	14	9.4
9	1.32 - 1.47	87.8	10	2.2	78.8	15	6.2	87.6	5	7.4
10	1.47 - 1.68	79.8	13	7.2	81.8	14	4.2	82.6	10	7.4
11	1.52 - 1.83	82.8	13	4.2	83.8	12	4.2	76.6	14	9.4
			11	6.2	85.8	10	4.2	81.6	13	5.4
13	2.83 - 2.98	82.8	12	6.2	87.8	5	7.2	88.6	5	6.4
14	2.18 - 2.34	81.8	12	6.2	71.8	20	8.2	76.6	8	15.4
15	2.34 - 2.49	71.8	18	10.2	71.8	18	10.2	76.6	18	5.4
16	2.54 - 2.69	81.8	12	6.2	81.8	14	4.2	76.6	14	9.4
17	2.69 - 2.84	83.8	11	5.2	85.8	10	4.2	69.6	24	6.4
18	2.84 - 2.99	81.8	12	6.2	75.8	18	6.2	78.6	16	5.4



<u>Figure 5.</u> Particle Size Distribution as a Function of Soil Depth. (Mean and S.D. of Eight* Post-Study Soil Cores - [*See Table 2.])

<u>Table 5.</u> Concentration of Pesticide Residues in Two Background Soil Cores Sampled Before the Study Began.

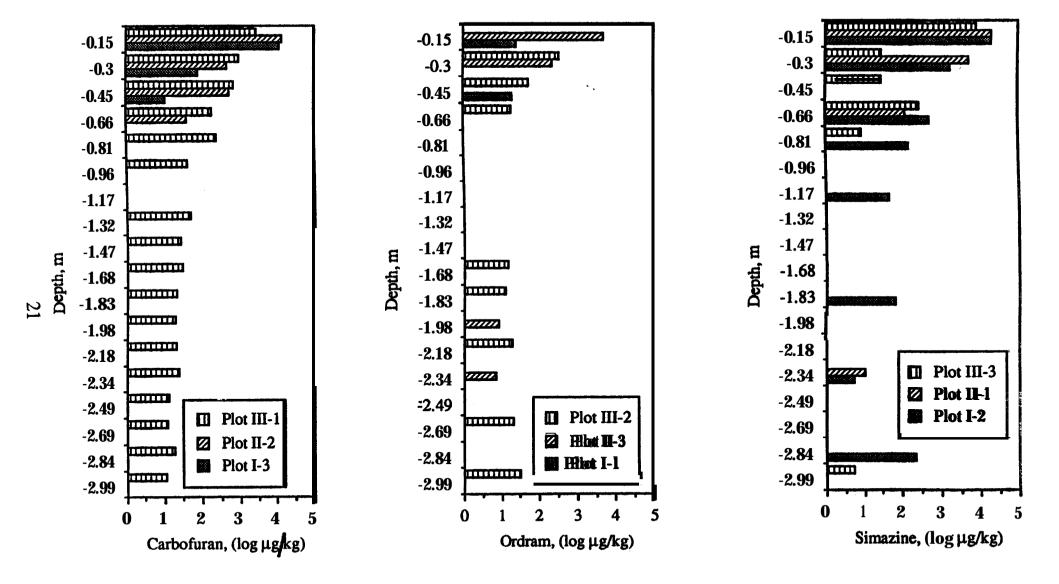
				<u>B-2</u>				
Sample #		Ordran	s Simazin	e Carbofuran	Ordram	Simazine	Carbofuran	
π	Depth, m				-μg kg ⁻¹	4-4-6	***	
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18	0.00 - 0.15 0.15 - 0.30 0.30 - 0.45 0.51 - 0.66 0.66 - 0.81 0.81 - 0.96 1.02 - 1.17 1.171.32 - 1.321.47 1.47 - 1.68 1.52 - 1.83 1.83 - 1.98 2.03 - 2.18 2.18 - 2.34 2.34 - 2.49 2.54 - 2.69 2.69 - 2.84 2.84 - 2.99	<20 <20 <10 <10 <10 <5 <10 <5 <10 <5 <10 <5 <10 <10 <10 <10 <10	<20 <20 <10 <10 <10 <5 <10 <5 <5 <5 <10 <5 <10 <10 <10 <10	<10 <10 <10 <10 <10 <10 <5 <10 <5 <5 <5 <5 <5 <10 <10 <10 <10 <10 <10	<20 <20 <10 <10 <10 <10 <10 <10 <10 <10 <10 <1	<20 <20 <10 <10 <10 <10 <10 <10 <10 <10 <10 <1	c10 <10 c10 <10 <10 <10 <10 <10 <10 <10 <10 <10 <	

[†] B-l and **B-2** refer to background cores 1 & 2 shown in Figure 1.

<u>Table 6.</u> Concentration of Pesticide Residues in Nine Soil Cores Sampled Upon Completion of the Study.

					I	Block # - Plot #	ŧ			
Sample	e	I-l Ordram†	I-2 Simazine†	I-3 Carbofuran [†]	II- 1 Simazine†	II-2 Carbofuran†	II-3 Ordram†	III- 1 Carbofuran§	III-2 Ordram§	III-3 Simazine†
#	Depth, m	*****		***************************************		μg kg ⁻¹				
1	0.00 - 0.15	26	21000	11000	20000	13000	4800	2700	c10	8200
2	0.15 - 0.30	<10*	1900	78	5400	440	230	910	330	31
3	0.30 - 0.45	21	-	11		510	<10*	680	57	30
4	0.51 - 0.66		520	<5	130	40	<5	180	19	280
5	0.66 - 0.81	<5	150	<5	<5	<5	<5	220	c10	8.8
6	0.81 - 0.96	<5	<5	<5 <5 <5	<5	<5	<5	40	<10	<5
7	1.02 - 1.17	<5	45	<5	<5 <5	<5 <5	<5	<10	<10	<5
8	1.17 - 1.32	<5	<5	<5	<5	<5	<5	46	<10	<5
9	1.32 - 1.47	<5	<5	<5 <5 <5	<5 <5 <5	<5 <5 <5	<5 <5	25	<10	<5
10	1.47 - 1.68	<5	<5	<5	<5	<5	<5	28	14	<5
11	1.52 - 1.83	<5	66	<5	<5	<5	<5	21	12	<5
12	1.83 - 1.98	<5	<5	<5	<5	<5	8.3	19	<10	8 <5
13	2.03 - 2.18	<5	<5	<5	10	<5	<5	21	18	<5
14	2.18 - 2.34	<5 <5 <5	5.2	<5 <5 <5	<5	<5	6.7	24	<10	<5
15	2.34 - 2.49	<5	<5	<5	<5	<5	<5	13	c10	<5
16	2.54 - 2.69	<5	<5	<5	<5	<5	<5	12	21	<5
17	2.69 - 2.84	<5	220	<5		<5	<5	18	<10	<5
18	2.84 - 2.99	<5		<5	<5	<5	<5	11	30	5.1

^{* =} Matrix interference reported.
- = Missing data
† = Drill-rig Sampler
§ = Bucket Auger Sampler



<u>FigDistri</u>bution of Pesticide Residues as a Function of Soil Depth (concentrations represented on a logarithmic scale)

<u>Table 7.</u> Quality Assurance Recovery Data Reported by ENSECO Laboratories.

SampleI.D.†		<u>Ordran</u>	1		<u>Simazine</u>		2	Carbofuran	
	spike Added	Recovery	Detection Limit	Spike Added	Recover	y Detection Limit	spike Added	Recovery	Detection Limit
	μg kg-l	%	μg kg ⁻¹	μg kg ⁻¹	%	μg kg ⁻¹	μg kg ⁻¹	%	μg kg ⁻¹
43-B-1 MS 43-B-1 MSD	200 200	75 80	20 20	200 200	80 90	20 20	200 200	70 105	10 10
43-B-2 MS 43-B-2 MSD	200 200	60 50	10 10	200 200	80 80	10 10	200 200	90 85	10 10
43-I-1/1 MS 43-I-1/1 MSD	100 100	94 84	5 5	-	-	•	•	-	•
43-I-2/1 MS 43-I-2/1 MSD	-	•	-	100 100	(a) (a)	5 5	-	-	•
43-I-3/1 MS 43-I-3/1 MSD	-	-	-	•	• •	 -	100 100	(a) (a)	5 5
43-II-1/8 MS 43-II-1/8 MSD	-	-	-	100 100	85 76	5 5	•	-	-
43-II-2/3 MS	-	•	-	-	-	•	100	70	5
43-II-3/6 MSD	100	69	5	-	-	-	•	•	•
43-III-2/7 MS 43-III-2/7 MSD	100 100	69 55	10 10	-	-	:	- -	-	- -
43-III-3/11 MS 43-III-3/1 1 MSD	<u>.</u>	- -	-	100 100	65 70	5 5	•	:	- -

^{† =} Study No.-Block # or Background-Plot #-Depth #
MS = Method Spike
MSD = Method Spike Duplicate
(a) = Spike recoveries obscured by high sample analyte levels.

spike recoveries (43-I-2/1 and 43-I-3/1), but no dilutions of these samples were reported. Concentrations of simazine and carbofuran residues in the upper 0.45 m of the soil cores were unexpectedly high, particularly in cores taken from plots I-2 and II-1 (simazine) and II-3 and II-2 (carbofuran) (Table 6). Mass balance calculations of these data indicate that between 2.2 and 6.6 times as much pesticide residue was found in these upper level samples than would have been expected (Table 8). Such calculations make the following assumptions:

- i. The pesticides, carbofuran, simazine, and **ordram** were applied in liquid form at a rate of **0.001kg ai.** m-2.
- ii. The pesticides were applied as uniformly as possible over each 9 m² plot using a hand held sprayer (see Materials and Methods).
- iii. Lateral movement of the pesticides in the surface sections was negligible, as rainfall infiltration rates were not exceeded, and no run-off was observed.

Under these assumptions, a value for the total amount of pesticide residue in each plot may be extrapolated from the data obtained from each of the soil cores. Table 8 indicates that although no more than 0.009 kg should have been recovered, reported simazine and carbofuran recoveries greatly exceeded this amount, with values of 0.025 and 0.032 kg for carbofuran, and 0.055 and 0.059 kg for simazine. In addition, some degradation over a 4 month period would be expected, since half-lives for these pesticides under aerobic soil conditions have been determined between 7 and 60 days for carbofuran, 8 and 160 days for **ordram**, and 10 and 300 days for simazine (CDFA, **1990**), which are in the same order of magnitude as the length of this study. Such extreme rates **o**: recovery **(286-360%** for carbofuran, and **613-655%** for simazine) suggest that problems in the determination of

<u>Table 8.</u> Mass Balance Calculations of Pesticide Residues in Nine Soil Cores Sampled Upon Completion of the Study.

	Block # - Plot #†									
	<u>I-1</u>	I-2	<u>I-3</u>	<u>II-1</u>	П-2	<u>II-3</u>	<u>III- 1</u>	III-2	III-3	
	Ordram	Simazine	Carbofuran	Simazine	Carbofuran	Ordram	Carbofuran	Ordram	Simazine	
Total Residue per Core, µg	32.98	35 1.60	7782.3	17924	9818.3	3540.6	3486.6	35 1.60	6009.5	
% Recovery per Core	3.51	614.7	286.6	655.6	359.1	129.5	127.5	12.86	219.8	
Extrapolated Total Residue per Plot, kg*	0.0001	0.055	0.025	0.059	0.032	0.011	0.011	0.001	0.019	

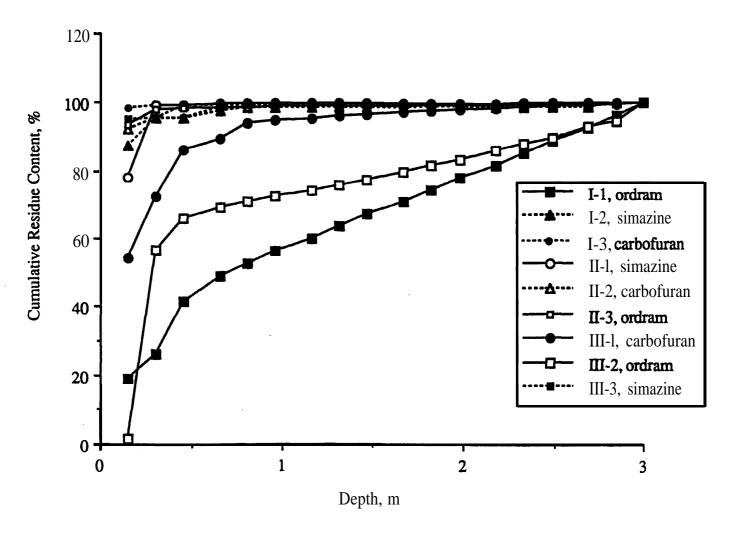
[†] See Fig. 1. * Should not exceed **0.009kg**

some of these samples may have been encountered, and that for the purposes of this study, these data should be considered, at best, qualitative.

However qualitative the data may be, the lack of pesticide residues detected in samples taken from below a depth of 0.66 m in the drill-rig sampled cores indicate that the bulk of the applied pesticide did not migrate beyond this depth. This is in agreement with the extent of mobility that might be expected to result from the relatively small amount of precipitation received (172 mm). In addition, the sporadic nature of the precipitation events, will affect the mechanisms which control pesticide behavior in soils, such as microbial- and **photo**-degradation, sorption onto soil surfaces, and volatilization. White et al. (1986) and Shipitalo et al. (1990) showed that prewetting the soil with a small pulse of precipitation may be sufficient to move pesticides into the surface layers of soil, thereby enhancing the effects of sorption and biological mechanisms, which would reduce the potential for transport during subsequent leaching events. The presence of macropores within the soil **profile** have been shown to be responsible for preferential transport of chemicals (Isensee et al., 1990, Shipitalo et al., 1990; White et al., **1986)**, and such phenomena may be responsible for the occurrence of isolated amounts of residue further down the soil profile of plot I-2 (Table 6).

Comparison of Sampling Techniques: Drill-rig vs. Bucket-Auger

With the exception of Block I plot 2 (simazine), only trace amounts of pesticide residue were detected below a depth of 1.17 m in the soil cores collected using the drilling rig. By comparison **carbofuran** and **ordram** residues were detected throughout the soil profile in the samples obtained using the bucket auger sampler. Examination of the cumulative concentrations of pesticide residues as a function of soil depth (Fig.7) where non-detected



FigCumulative Concentrations of Pesticides as a Function of Soil Depth

values were taken as zero, indicate that cores from plots III-2 (ordram) and III-1 (carbofuran) contained a significant portion of the total amount of residue recovered below a depth of 0.66 m. Although the distribution of ordram residue in plot I-1 would also seem to indicate this, it is important to note that pesticide residue concentrations observed in this plot were lower than amounts reported for the other eight plots (Table 6.).

Since only plots which had received **ordram** and carbofuran were sampled using the bucket-auger, the two sampling methods were compared to evaluate differences between the mean concentrations of these two pesticides within the sections of soil core. A comparison was performed in order to determine if the differences in pesticide concentration in the soil profiles resulted from the choice of sampling method. The experimental plots were spatially close and subject to equal amounts of precipitation, and so similar pesticide migration rates for each plot, resulting from the precipitation, may be assumed. Differences in organic carbon content and amounts of sand, silt, and clay, which could cause the compounds to concentrate in particular sections, were partitioned out by comparing all sample cores, with a 0.15 m section as the sample unit. This results in the partitioning of the section variability into the error term. Significantly higher pesticide residue concentrations at depth in the soil profile would be an indication of cross contamination of lower sections by one of the sampling methods. If, however, no significant difference between the sampling methods is found, the result may be indicative that either no cross-contamination or equal cross-contamination has occurred, because this is a test for difference in means.

The first three sections of each soil core have been omitted from the analysis for several reasons. Firstly, because the pesticides were applied to the soil surface, the first three 0.15 m sections were not subjected to the same contamination processes as the sections farther down in the soil profile. Secondly, as previously discussed, the first **three sections were**

found to have recovery rates of up to 600% of the applied amounts of the two compounds, and, therefore, may be of questionable validity. Thirdly, the drill-rig takes soil samples 0.45 m at a time (**Fig.2**), and so the first three sections are all from the first sample and could have been contaminated by the passage of the drill through the soil surface. In addition, the variance in pesticide residue concentrations found in the first three sections is much higher than for the rest of the sections, and even after the use of variance reducing transformations still obscure the differences in the lower sections which are more important for our purposes.

Differences were tested with a one-way ANOVA for each of the two compounds (carbofuran and ordram) comparing all the drill-rig samples with all the bucket-auger samples, and on a core by core comparison with t-tests. The unpaired t-test was used because differences in organic carbon content and other soil factors within the soil core sections made the use of a paired comparison by depth incorrect. The t-tests were run as a check, because the observed differences in variance of the sections between sampling methods could lower the precision of the ANOVAs. Both the t-tests and the ANOVAs gave the same result, so variance equalizing transformations were deemed unnecessary (Table 9).

The one way **ANOVAs** both show significantly higher concentrations in the bucket-auger samples than in the drill-rig samples. For carbofuran the overall average concentration is 1.3 µg kg⁻¹ in the drill-rig samples and 45.2 µg kg⁻¹ in the bucket-auger samples. For the **ordram** there is also a significantly higher contamination level in the bucket-auger samples with a mean of 7.6 µg kg⁻¹ versus a mean of 0.5 µg kg-f for the drill-rig samples. The tests also show a significantly higher concentration on a core by core comparison. The soil variables are similar for all of the cores, but the drill-rig samples display virtually no contamination below the first three 0.15 m samples. This indicates that there is significant

<u>Table 9.</u> ANOVA and T-Test Results For Differences Between Drill Rig and Bucket-Auger Methods of Soil Sampling

ANOVA

Carbofuran

Source	df	Mean Square	F	p-value
Sampler	1	19242.844	13.93	.0006
Error	43	1381.467		

Group	Count	Mean	Standard Deviation
Drill Rig	30	1.333	7.303
Bucket Auger	15	45.2	64.285

Ordram

Source	df	Mean Square	<u> </u>	<u>p-value</u>
Sampler	1	504.1	13.505	.0007
Error	43	37.328		

Group	Count	Mean	Standard Deviation
Drill Rig	30	.5	1.907
Bucket Auger	15	7.6	10.35

T-TEST

Drill-Rig	VS	Bucket-Auger	Significance
Carbofuran 1		Carbofuran	.011
Carbofuran 2		Carbofuran	.017
Ordram 1		Ordram	.0082
Ordram 2		Ordram	.0237

cross-contamination down through the hole of the bucket-auger samples for both compounds. Since it is virtually impossible to insert the bucket auger into the hole without touching the walls, soil is easily dislodged from the upper levels, and falls down the hole to be incorporated into the lower samples.

Conclusions

A qualitative appraisal of the data indicates that the mobility of pesticide residues in soils which receive a relatively low precipitation component was limited, and confined to the upper portions of the soil profile.

The use of a bucket-auger in dry, easily friable soils (such as encountered in this study) is not recommended, since cross-contamination between samples from the same core may occur as a result of dislodged soil material being incorporated into samples taken from deeper within the soil profile.

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Appendix A

copy of

the

1986 Protocol by R.R. Teso, M. Peterson, R.E. Gallavan and D.L. Sheeks, III.

"Seasonal Rainfall effects on Pesticide Leaching"

SEASONAL RAINFALL EFFECTS ON PESTICIDE LEACHING (RIVERSIDE PROTOCOL)

Objective:. The purpose of this investigation is to characterize the effects of seasonal rainfall on the distributions of three surface-applied pesticides within the soi 1 'profile.

Procedure: Two undisturbed soil cores (10 foot depth in 6 inch increments) will be extracted from between each of three 38-foot long blocks in an area designated as a 6 foot buffer zone (see plot 1 ayout). The cores are to be extracted the week of the 18th of November. The soi 1 samples will 1 be packed in dry ice and transported to the CDFA chamber site for storage and further processing. The core samples will then be split and a sub-sample sent to CAL-LABS in Sacramento for residue analysis for carbofuran and ordram content. Simazine analysis will be performed by Laboratory Services of CDFA.

Three blocks will be set up lengthwise in line with the previously sampled background sites. The blocks wi 11 be 38 feet in length and will consist of three 18-foot plots with 4-foot buffer separations. Adjoining blocks will be separated by 6-foot buffer regions, Initial plot preparation will include leveling of the surface in an attempt to minimize runoff or ponding problems. The field will be irrigated and allowed to drain to field capacity within one week of background core extraction and pesticide

application, Furrows will be raised at the head end of the field and along the sides of the plots to exclude irrigation and rainfall runoff effects from surrounding grounds.

One of the three'pesticides simazine, carbofuran and ordram will.

be applied to an individual plot in each block selected at random

at rates equivalent. to 10 pounds.active ingredient per acre using

hand sprayer's where applicable. granular materials will be

broadcast on surface of the plot and raked in. An equivalent

amount of water will be hand sprayed on the surface (20 gal 1 ons of water per acre).

Precipitation will be measured with two plastic rain guages located on-site adjacent to the plots. Guages will be capable of registering rainfall in 1/100 inch increments. Rainfall event information will be recorded in a log book and will include event dates, recording dates, quantity and the name of person taking readings.

At the conclusion of the rainfall season <in Riverside about mid-April) one soil core will be extracted from each plot along a transect line established by the background core sites.

Capproximately the center of the plots). Soi 1 core samples will be processed as for the background samples, i.e. residue analysis and soi 1 parameters.

Resultant data will be analyzed with Analysis of Variance and Contingency Table Analysis. It will also be displayed graphically as transect results and compared to Fresno study results if

Appendix **B**

Chain of Custody Record

. STATE OF CALIFORNIA DEPARTMENT OF FOOD AND AGRICULTURE

CHAIN OF CUSTODY RECORD (use ball point pen only)

ENVIRON. HONITOR. & PEST MONT. ENVIRON. HAZARDS ASSESSMENT 1220 N STREET, ROOM A-149 SACRAMENTO, CA 95814

Study #		at	on	ple #	(inches)			flo	Date Collected Time				Leng (inch	Segment of tength (inches)			Cylind Tare Wei (grams		right	
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Soil Gross Wei (grams)	_						-		units			9	2110	د اسونسس		Units	\$ oistu	re	Lab	
1163																	·	Ц	Ш	
41 42 43 44	45	46	47	48 49 50 5	1 52 53 54	55 56	57 58	59 60 6	1 62 (53 64	65 66	67 6	8 69 70	71 72	2 73	74 75	76 77	78 7	9 60	
Cyllinder	# ;	/ I°	? /	Luu	atiun:				Lab	Kesul	ts: ¿	leu	kg	-(q	pb.) Sa	ve (EXT	acts	
Remarks:									Sin	zine										
									C iyk	(defura	an									
									Ordr	am		くし	0							
Core #:				KEY				- : ₍	Chemi	st:	AL9	et	-			Da	م te:	اما	96	
<u>Col. 1:</u> S = Spike				<u>Co)</u>	. 7: Backgroun COTE #1	d Core	•		nquist ynatur	ed for	Lab t	by:	Date	/Time	•					
<u>Col. 2:</u> • = Split				2 =	Core #2				_	y: (Sig		e) 1	Relinqui W. F				re)	Date/1 9/13	lime	
Col. 5:					Core #3			ece	ived t	y: (Sig	natur	e)	telinqui	shed	by: (S	ignatu		Dete/	Time	
F = Fresno R = Ri vers				\$ =	: 33: Simazine			Rece	ived t	y: (Sig	natur	e) [Pelinqui	shed	by: (S	ignatu	re)	Bate/	ine	
<u>Col. 6:</u>	- 40				Carbofura Ordran	n.		7 200	iver t	y: (Sig	natur	A Ca	elinqui	shed t	w: (\$	ionatu	e)	Dete/	ine	
1 = Plot # 2 = Plot#					<u>. 79-60:</u>			/ NEUG	-14EU [y. (318	, or will	·/ "	- and a supple		. y . \u					
3 = Plot #	3				= Food & A = Cal Labs				iveo +			Ŧ		190	272	Lab				
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